

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE Sept. 9, 1996	3. REPORT TYPE AND DATES COVERED Technical Report #19		
4. TITLE AND SUBTITLE Electrically Generated Intramolecular Proton Transfer: Electroluminescence and Stimulated Emission in Polymers		5. FUNDING NUMBERS N00014-94-1-0540		
6. AUTHOR(S) R.M. Takka, X. Zhang and S.A. Jenekhe		Kenneth J. Wynne R & T Code: 3132111		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemical Engineering University of Rochester 206 Gavett Hall Rochester, NY 14627		8. PERFORMING ORGANIZATION REPORT NUMBER # 19		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Accepted for Publication in <i>Journal of the American Chemical Society</i>				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Application of a voltage across a thin film of a rod-coil copolymer containing 2-(2'-hydroxyphenyl)benzothiazole in the backbone induces a reversible intramolecular proton transfer. The observed electroluminescence occurs from the excited keto form, produced electrically by a novel chemical reaction termed <i>electrically generated intramolecular proton transfer</i> , EGIPT. Stimulated emission between 540-640 nm was observed by ps transient absorption spectroscopy. EGIPT and related proton transfer electroluminescence have implications for understanding proton transfer reactions and organic light emitting devices.				
14. SUBJECT TERMS Proton transfer electroluminescence; stimulated emission; light-emitting devices; population inversion; polymers.		15. NUMBER OF PAGES 12		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

19960925 127

OFFICE OF NAVAL RESEARCH

GRANT N00014-94-1-0540

R&T Code 3132111

Kenneth J. Wynne

Technical Report No. 19

Electrically Generated Intramolecular Proton Transfer: Electroluminescence and Stimulated Emission in Polymers

by

Richard M. Tarkka, Xuejun Zhang and Samson A. Jenekhe

Accepted for Publication

in

Journal of the American Chemical Society

University of Rochester
Department of Chemical Engineering
Rochester, NY

September 9, 1996

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale;
its distribution is unlimited

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (1)
Chemistry and Physics Division
Ballston Tower 1, Room 503
100 North Quincy Street
Arlington, Virginia 22217-5660

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Kelvin Higa (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Peter Seligman (1)
Naval Command, Control and
Ocean Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Electrically Generated Intramolecular Proton Transfer: Electroluminescence and Stimulated Emission from Polymers

Richard M. Tarkka,¹ Xuejun Zhang, and Samson A. Jenekhe*

Department of Chemical Engineering and Center for Photoinduced Charge Transfer,
University of Rochester, Rochester, New York, 14627-0166

Abstract

Application of a voltage across a thin film of a rod-coil copolymer containing 2-(2'-hydroxyphenyl)benzothiazole in the backbone induces a reversible intramolecular proton transfer. The observed electroluminescence occurs from the excited keto form, produced electrically by a chemical reaction termed *electrically generated intramolecular proton transfer*, EGIPT. Stimulated emission between 540-640 nm was observed by ps transient absorption spectroscopy. EGIPT and related proton transfer electroluminescence have implications for understanding proton transfer reactions and organic light emitting devices.

¹ Address after August 1, 1996: Department of Chemistry, The George Washington University, 725 21st St. N.W., Washington, D.C. 20052

The combination of electrochemically generated radical cations (positive polarons) and radical anions (negative polarons) in solution to generate light is known as electrochemiluminescence,¹ a process known for more than 30 years.² Exploration of similar processes in organic solids, using small molecules³ or polymers such as poly(p-phenylenevinylene)⁴ as the active media, has resulted in the development of organic light emitting diodes (LEDs). Among the challenges facing development of organic polymers as LED materials are those of stability, processibility, efficiency, questions of mechanism, and the drive to develop organic polymers for electrically driven diode lasers.^{5,6} Herein we report an electroluminescent single component copolymer which is soluble and processible from organic solvents, and in which the emissive component is photostabilizing and displays stimulated emission. The mechanism of electroluminescence is *electrically generated intramolecular proton transfer* (EGIPT), a chemical reaction which has not previously been reported.

Materials which exhibit excited state intramolecular proton transfer^{7,8} (ESIPT, Scheme 1) have been extensively studied as photostabilizing materials and as laser dyes.⁹ Intramolecularly hydrogen bonded heterocyclic molecules such as 2-(2'-hydroxyphenyl)benzothiazole, **1**, exist exclusively in the enol form (E) in the ground state. Upon photoexcitation, tautomerization occurs in the sub-picosecond time regime to generate the excited keto form (K*).^{10,11} Emission from K* occurs with a large Stokes shift. Moreover, a population inversion occurs facilitating stimulated emission.⁸

It occurred to us that polymers which incorporate intramolecularly hydrogen bonded moieties such as **1** in the main chain might lead to electroluminescent materials which have photochemical stability, resistance to thermal degradation, and low self-absorption, if they both exhibit ESIPT and fluoresce. Such materials might address issues of photochemical stability needed for development of polymer light sources.

Copolymers which incorporate intramolecularly hydrogen bonded moieties as side chains have previously been reported. Vogl and coworkers¹² and Scott and coworkers¹³

have investigated the photostabilizing effects of 2-(2'-hydroxyphenyl)benzotriazole derivatives covalently attached to various polymers. Acuna and coworkers¹⁴ reported that copolymers of poly(methyl methacrylate) which incorporated 2-(2'-hydroxyphenyl)benzimidazole derivatives could be fabricated into optically pumped solid state proton transfer laser materials.

Our studies on main-chain polymers containing 2-(2'-hydroxyphenyl)benzoxazole (HBO) and related moieties in the main chain showed that ESIPT in polymers is complicated by the effects of concentration quenching, extended conjugation and competition with excimer formation.¹⁵ Excimers and exciplexes have previously been observed in conjugated polymers such as poly(p-phenylene benzobisthiazole), a phenomenon which substantially decreases the photoluminescence quantum yield.¹⁶ On the other hand, a detailed study of rod-coil copolymers showed that the detrimental effects of excimer formation on emission yields could be regulated by introducing flexible segments into the main chain, which prevented the rigid segments from aggregating, favorably changing the supramolecular assembly of the fluorophores in the solid state.¹⁷

The structure of the random copolymer, poly(benzobisthiazole-1,4-(2-hydroxy)phenylene)-*co*-poly(benzobisthiazoledecamethylene), HPBT-*co*-PBTC10 (5% HPBT/ 95% PBTC10), used in this study is given by **2**. A copolymer with 5 % active component was chosen for investigation since the copolymer is soluble in formic acid, the average conjugation length is sufficiently short that ESIPT is not inhibited,¹⁵ as in the case of the HBO homopolymer, and because excimer formation is inhibited by the supramolecular structure of the copolymer.¹⁷ The copolymer **2** was prepared from DABDT (TCI or Daychem), hydroxyterephthalic acid¹⁸ and 1,10 decanedicarboxylic acid by condensation reaction in polyphosphoric acid as previously described.¹⁷ Films were prepared by spin coating a 1% w/w solution of the polymer in formic acid onto the appropriate optical window.

To prepare the LED device, a layer about 500 Å of poly(vinyl carbazole) (PVK) was deposited by spin coating from chloroform solution onto an ITO (indium tin oxide) coated glass substrate. The PVK layer functions as the hole transporting layer and electron blocking barrier to confine electrons to the emissive layer. A 500 Å emissive layer of **2** was spin coated from a formic acid solution and dried at 80 °C in a vacuum oven. An electron injecting aluminum electrode of *ca.* 500 Å was thermally evaporated at a vacuum of 4×10^{-6} torr. The structure of the LED device is shown in Figure 1 (inset).

Measurements were performed under ambient conditions. Optical absorption measurements were done using a Perkin-Elmer Lambda-9 UV/vis/near-IR spectrophotometer. Photoluminescence and electroluminescence spectra were measured using a Spex Fluorolog-2 spectrofluorimeter. The transient absorption spectrum was recorded using a pump wavelength of 355 nm and a 50 ps delay.¹⁹ Correction for ambient lighting was made by subtracting the spectrum obtained when neither a pump pulse nor a probe pulse passed through the sample, whereas sample fluorescence was corrected for by subtracting the spectrum obtained by passing a pump pulse (with no probe pulse) through the sample.

Figure 1 shows the UV spectrum of a thin film of **2** together with the photoluminescence (PL) and electroluminescence (EL) spectra. Both the PL and EL spectra have a strong emission band at 543 nm, with very weak bands at shorter wavelengths. The PL quantum yield for emission is 6-12 % for copolymers with 5-10 mol % HPBT. The origin of the minor bands is not from the PVK layer which emits at 430 nm,²⁰ but is probably normal enol emission from the E* state (Scheme 1).²¹ It has previously been demonstrated that extended conjugation inhibits ESIPT and leads to enol emission due to an increase in the energy barrier on the excited state potential energy surface.¹⁵ The conjugation length of the shortest fluorophore in **2** which is capable of existing in the keto form is 10 double bonds, twice as long as **1** for which there is no such barrier. It is possible that there is a small potential energy barrier to proton transfer on the

excited state potential energy surface of **2**, leading to incomplete proton transfer and emission from both E* and K* (Scheme 1).

The PL and EL peak at 543 nm clearly arises from emission of the excited keto tautomer (K* in Scheme 1). Evidence for this assignment is as follows: (1) the large Stokes shift between the emission band and the absorption band is typical of ESIPT processes leading to the keto state, a process very well known to occur for intramolecularly hydrogen bonded molecules structurally similar to the HPBT component of **2**.^{7,8} In contrast, the corresponding 5 % copolymer without hydroxy side groups, which is not capable of ESIPT, has a much smaller Stokes shift, with the emission λ_{max} occurring at 486 nm.¹⁷

(2) The transient absorption spectrum of **2** shown in Figure 2 has a region of optical gain (stimulated emission) between 540 nm and 640 nm. The keto form K does not initially exist in the ground state, so formation of K* after excitation leads to a population inversion, facilitating the observed stimulated emission. This phenomenon has been well documented in the case of molecules structurally similar to the HPBT component of **2**.^{7,8,9}

The mechanism of formation of K* by photoexcitation is well documented^{7,9} to occur by a rapid proton transfer in the E* form. In the case of EGIPT, injection of electrons and holes will lead to immediate formation of enol radical anions and enol radical cations. These radicals might undergo electron transfer to form E*, which would lead to the observed results. However, more experimental evidence is needed before other plausible mechanisms can be definitively ruled out.

EGIPT and related proton transfer electroluminescence, which are demonstrated here, have implications for understanding proton transfer reactions and organic light emitting devices. For example, theoretical predictions of the effects of an electric field on tunneling in proton transfer reactions²² might now be tested with EGIPT. The device architecture and proton transfer copolymer of the LED discussed here represent unoptimized initial results. Current- and luminance-voltage measurements indicate a turn-on voltage of 12 V and a luminance of *ca.* 1 cd/m² at a current density of 12 mA/cm².

Optimization of device parameters should significantly increase the performance of EGIPT-based LEDs.

Acknowledgments. This research was supported by the Office of Naval Research and in part by the National Science Foundation (CTS 9311741, CHE-9120001). We thank E. Gaillard for technical assistance with the picosecond transient absorption spectroscopy measurements.

References and Notes

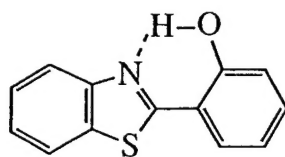
1. Debad, J.D.; Morris, J.C.; Lynch, V.; Magnus, P.; Bard, A.J. *J. Am. Chem. Soc.* **1996**, *118*, 2374-2379.
2. Knight, A.W.; Greenway, G.M. *Analyst* **1994**, *119*, 879-890.
3. Tang, C.W.; Van Slyke, S.A. *Appl. Phys. Lett.* **1987**, *51*, 913-915.
4. Burroghes, J.H.; Bradley, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burn, P.L.; Holmes, A.B. *Nature* **1990**, *347*, 539-541.
5. Graupner, W.; Leising, G.; Lanzani, G.; Nisoli, M.; De Silvestri, S.; Scherf, U. *Phys. Rev. Lett.* **1996**, *76*, 847-850.
6. Yan, M.; Rothberg, L.J.; Papadimitrakopoulos, F.; Galvin, M.E.; Miller, T.M. *Phys. Rev. Lett.* **1994**, *72*, 1104-1107.
7. See the special issues: *Chem. Phys.* **1989**, *136*, 153-360; *J. Phys. Chem.* **1991**, *95*, 10215-10524.
8. Formosinho, S.J.; Arnault, L.G. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 21-48.
9. Khan, A.U.; Kasha, M. *Proc. Natl. Acad. Sci. USA* **1983**, *80*, 1767-1770.
10. Laermer, F.; Elsaesser, T.; Kaiser, W. *Chem. Phys. Lett.* **1988**, *148*, 119-124.
11. Frey, W.; Laermer, F.; Elsaesser, T. *J. Phys. Chem.* **1991**, *95*, 10391-10395.
12. Nir, Z.; Vogl, O. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 2735-2754.
13. O'Connor, D.B.; Scott, G.W.; Coulter, D.R.; Gupta, A.; Webb, S.P.; Yeh, S.W.; Clark, J.H. *Chem. Phys. Lett.* **1985**, *121*, 417-422.
14. Ferrer, M.L.; Acuna, A.U.; Amat-Guerri, F.; Costela, A.; Figuera, J.M.; Florido, F.; Sastre, R. *Appl. Opt.* **1994**, *33*, 2266-2272.
15. Tarkka, R.M.; Jenekhe, S.A. *Mat. Res. Soc. Symp. Proc.* **1996**, *413*, 97-102.
16. Jenekhe, S.A.; Osaheni, J.A. *Science* **1994**, *265*, 765-768.
17. Osaheni, J.A.; Jenekhe, S.A. *J. Am. Chem. Soc.* **1995**, *117*, 7389-7398.

-
18. Miura, Y.; Torres, E.; Panetta, C.A. *J. Org. Chem.* **1988**, 53, 439-440.
 19. Osaheni, J.A.; Jenekhe, S.A.; Perlstein, J. *J. Phys. Chem.* **1994**, 98, 12727-12736.
 20. Hu, B.; Yang, Z.; Karasz, F.E. *J. Appl. Phys.* **1994**, 76, 2419-2422.
 21. An identical photoluminescence spectrum of **2** was obtained without PVK in the sample.
 22. Morillo, M.; Cukier, R.I. *J. Chem. Phys.* **1993**, 98, 4548-4556.

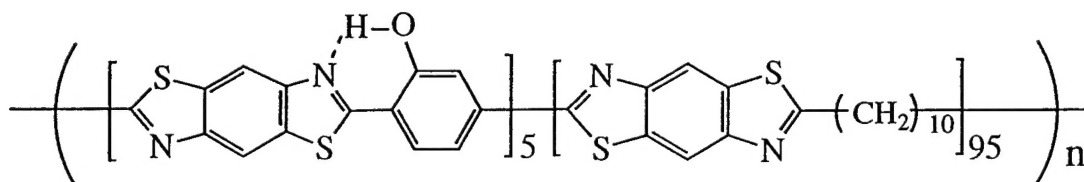
Figure Captions.

Figure 1: Normalized UV \blacklozenge , Electroluminescence \circ (12 V), and Photoluminescence \bullet ($\lambda_{\text{ex}} = 396 \text{ nm}$) spectra, of a thin solid film of HPBT-co-PBTC10 (5 % HPBT/ 95 % PBTC10); 2.

Figure 2: Transient absorption spectrum of a thin solid film of HPBT-co-PBTC10 (5 % HPBT/ 95 % PBTC10); 2. Delay = 50 ps, $\lambda_{\text{ex}} = 355 \text{ nm}$.

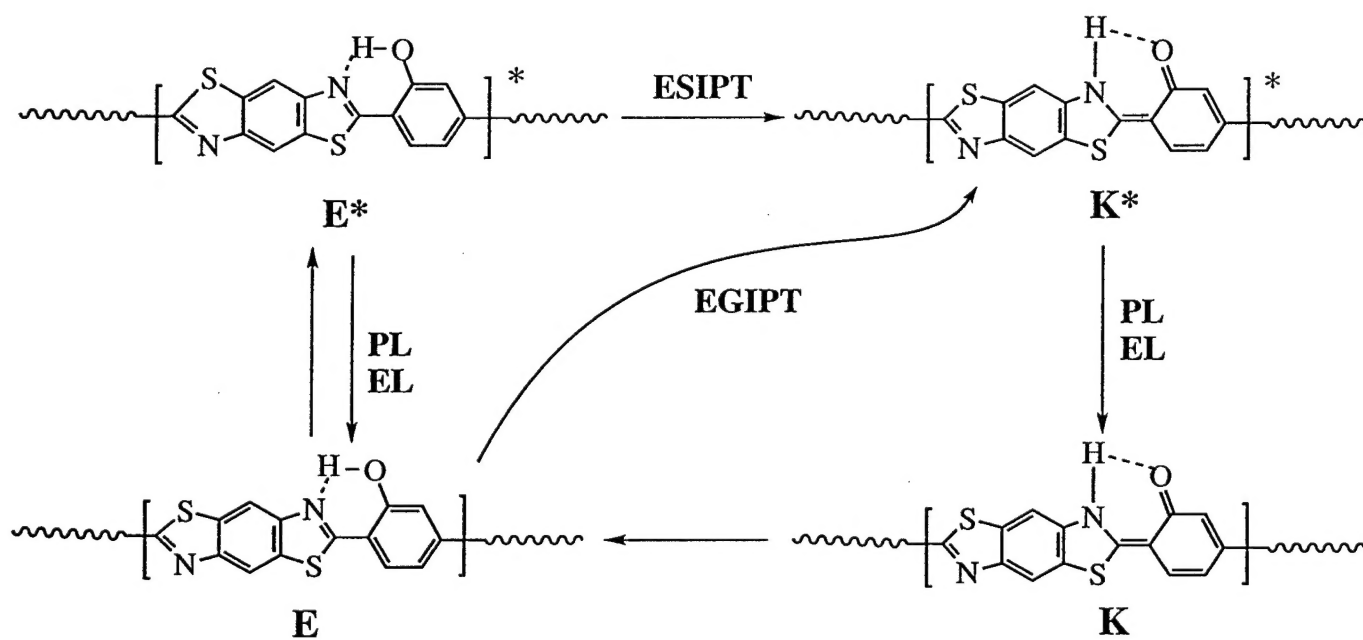


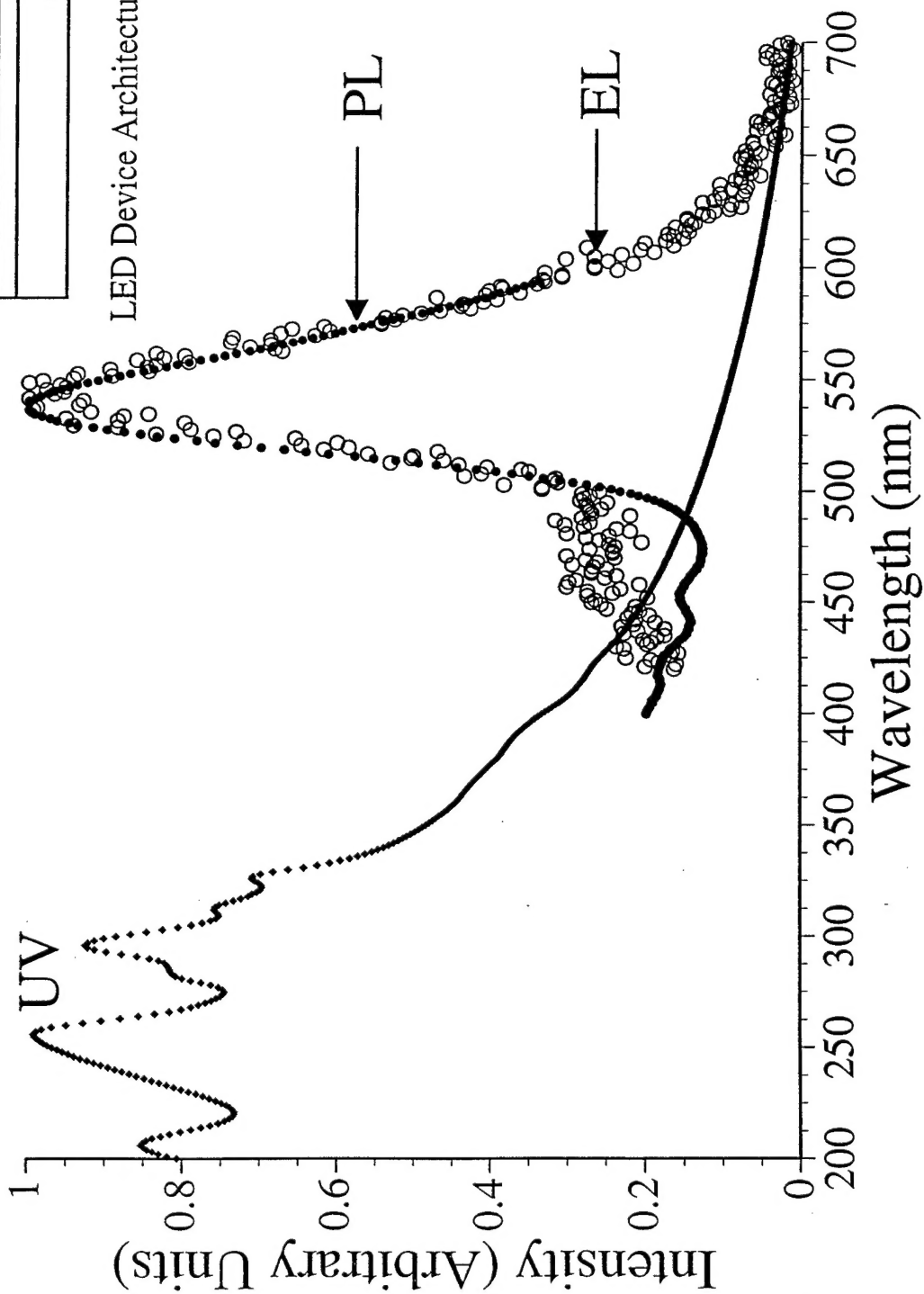
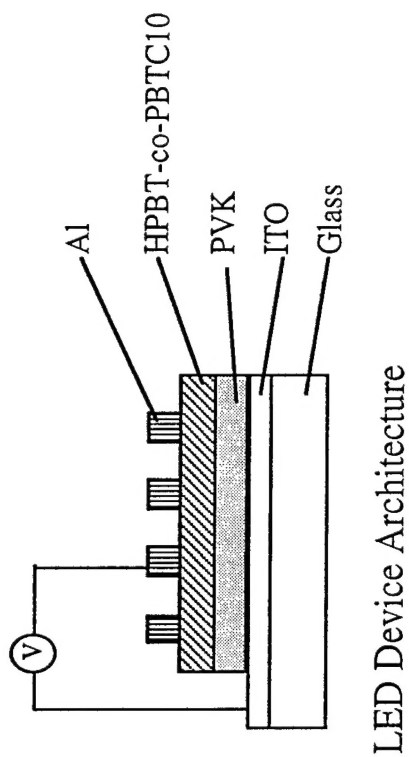
HBT, 1



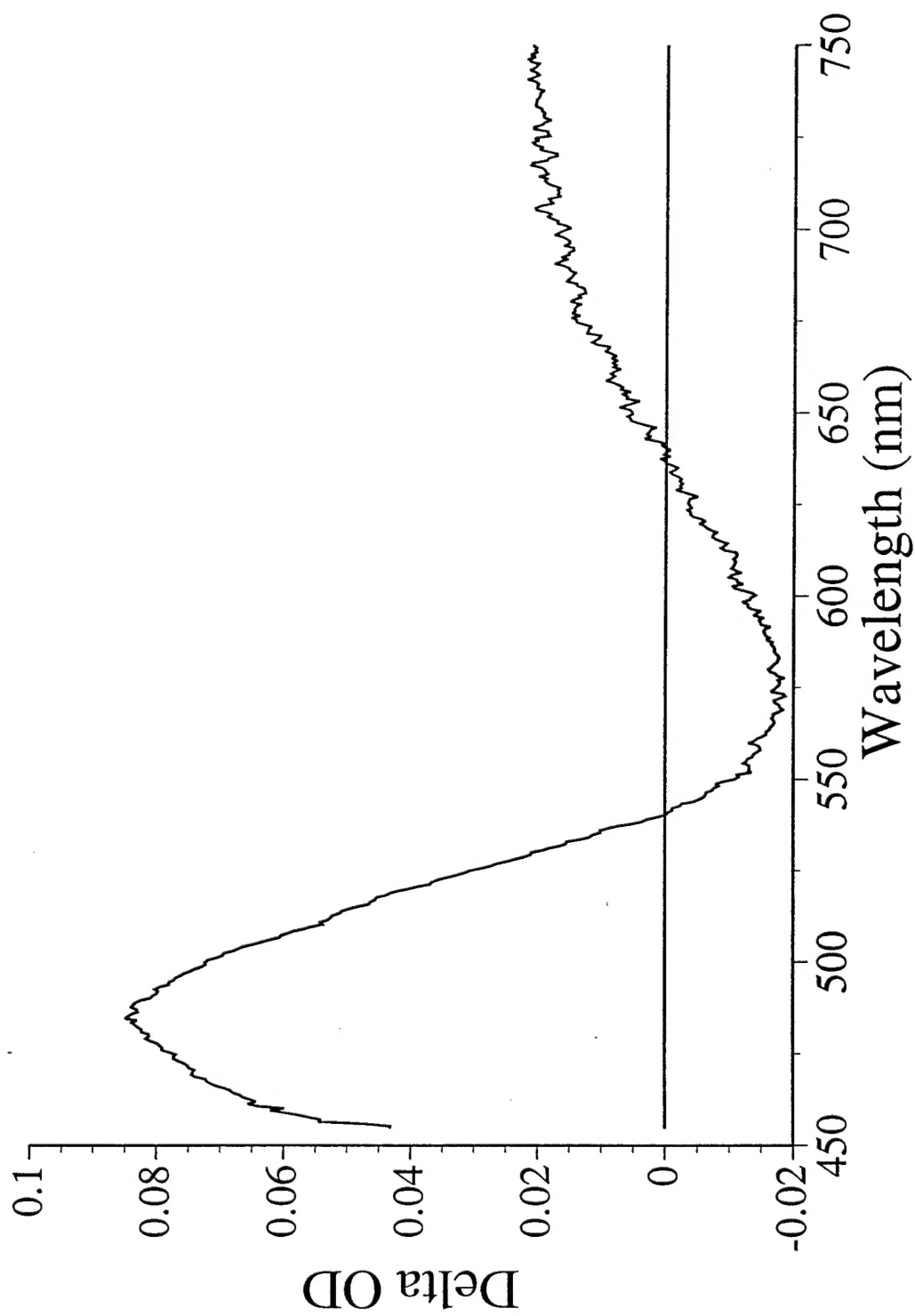
HPBT-co-PBTC10 (5/95), 2

Scheme 1





TAKEDA ET AL
FIGURE 1



TABULA 6 AL
FIGURE 2